

REPORT DOCUMENTATION PAGE

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14. ABSTRACT We have developed a new class of polypyrroles bearing both hydrogen-bond acceptor and hydrogen-donor groups such that the intramolecular hydrogen bonding holds the system planar enhancing conjugation. The presence of other hydrogen-bond acceptors causes a disruption in this effect. Strong solvatochromic shifts occur to the blue in this case. As part of our attempt to improve on the synthesis of the monomer, we have exploited microwave assisted Diels-Alder reactions to form the heterocyclic monomer.					
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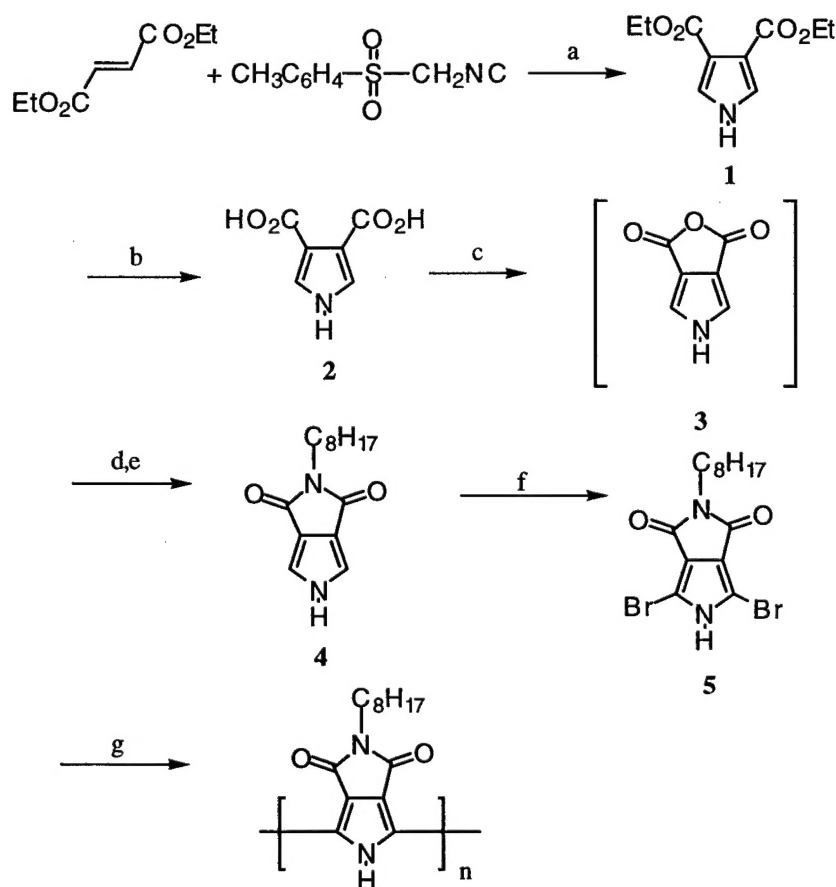
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Final Technical Report

This project constituted the masters thesis of Mr. Bethuel Kgobane and collaboration with D. Yousef Hijji of Morgan State University. The results of the first synthesis of the the oligomeric intramolecular polypyrroles.

S. K. Pollack, Y. M. Hijji and B.L.Kgobane, Poly(2-alkylpyrrolo[3.4-c]-1,3-(2H,5H)-dioxopyrrole-4,6-diyl)s. A Novel Class of Intramolecularly Hydrogen-Bonded Conjugated Polymers., *Macromolecules*, **30**(21),6709,1997.



GPC and NMR results reveal that this material is oligomeric, with an average DP of 8. Solvatochromism is observed.

Experimental

Starting materials were obtained from commercial sources and unless otherwise

specified, were used as supplied. Solvents were purified via standard methods. All

melting points were obtained using a Fisher-Johns melting point apparatus and are uncorrected. NMR spectroscopy was performed on a GE QE-300 NMR spectrometer equipped with a TecMag data system. Infrared spectroscopy was performed using a Perkin-Elmer Model 1600 Fourier transform infrared spectrometer. Gel permeation chromatography was performed on an instrument consisting of a Knauer RI, and GBC UV/Visible detector (tuned to 300 nm) and GPC pump, a Rheodyne injector, a 300 mm x 7.5 PL-E-Linear Column and PE-Nelson Model 900 data interface and data and collection software written in house. Samples were eluted in toluene. UV/visible spectra were obtained using a Beckman DU 7 spectrophotometer. Mass spectra were obtained using either a Finnegan Model 3500 GC/MS system or a Hewlett-Packard Model 5989 GC/MS. Number average molecular weights were obtained via end group analysis utilizing ^{13}C NMR. Molecular modeling was carried out on a Silicon Graphics Indigo² workstation using Spartan (Wavefunction, Inc., Irvine, CA) and Cerius² (Molecular Simulations, Inc., Waltham, MA).

3,4-diethylpyrrole dicarboxylate (1) To a suspension of 11.5 g (102.6 mmols) of potassium t-butoxide in 100 mL of anhydrous THF (distilled from Na/benzophenone) under N_2 atmosphere at room temperature in a 3-neck round bottom flask equipped with a condenser, addition funnel and a rubber septum, was added a solution of 10.0 g (51.2) mmol of tosyl methyl isocyanide and 8.8 g (51.2 mmol) of diethylfumarate in 50 mL of anhydrous THF dropwise from an addition funnel. Upon the addition of the mixture in the addition funnel, the solution turned red with the formation of a precipitate, and the solution became warm. At this stage, a water bath was used to moderate the temperature.

When the addition was complete (about 1 hour), the flask was taken out of the water bath and stirred at room temperature overnight. To the deep red solution was added saturated aqueous NaCl and the mixture was transferred to a separatory funnel and extracted with two 50 mL portions of THF. The organic layers separated were combined and dried over anhydrous magnesium sulfate. Filtration and solvent removal under vacuo (rotary evaporator) gave a dark red residue which was dissolved in methanol. Water was added to the methanol solution until a precipitate formed. Cooling and filtration gave a creamy filtrate that was washed with excess water. The resulting solid was air dried and then dried in vacuo to give 6.4 g (59% yield) of clear crystals. m.p. 150-152°C;

δ -¹H (DMSO-d₆) : 11.77 (1 H broad s), 7.36 (2H), 4.167 (4H, Q, J= 6.59 Hz), and 1.223 (6 H, t, J= 6.59 Hz); δ -¹³C (CDCl₃): 164.26, 126.02, 115.69, 60.18, 14.25; IR(KBr): 3270.5, 2982.6, 1715.3, 1437.7, 1288.6, 1058.2, 813.7, 764.0, 609.8, 530.6

3,4-pyrrole dicarboxylic acid (2) 5.4 g of **1** (25.6 mmol) were added to a solution of NaOH 8.0 g in 80 ml of 50% (v/v) aqueous ethanol. After stirring, the mixture was heated to reflux for 2 hours. While the solution was hot, water was added to the mixture and then acidified with 10% HCl solution. A white precipitate formed that was collected by filtration and washed with water. The solid was air dried then dried in vacuo to give 2.90 g (75% yield) m.p. > 300 C with decomposition. δ -¹H (DMSO-d₆) 12.15 (2H, br S), 7.60 (2H, d, J= 2.93 Hz); δ -¹³C (DMSO-d₆) 164.35, 126.09, 111.90; IR(KBr): 3121.9, 3086.9, 2965.9, 1673.8, 1566.3, 1521.3, 1385.8, 1308.7, 1238.1, 1206.6, 1158.3, 1091.9, 1070.7, 886.2, 747.5, 606.7, 520.4 cm⁻¹

4-(Octylcarbamoyl)pyrrole-3-carboxylic acid (4) N,N'-dicyclohexylcarbo-diimide (4.4 g 21.3 mmol) dissolved in 30 mL anhydrous THF under N₂ atmosphere at room temperature was added in one portion to a slurry of 2.75 g (17.7 mmol) **2** in 20 mL of THF, the mixture was stirred and refluxed for 2 hours at which time a precipitate had formed. The mixture was cooled to room temperature and filtered to remove the N,N'-dicyclohexylurea, which was washed with more THF. The combined THF solutions of **3** (1-aza-7-oxa-bicyclo[3.3.0]octa-2,4-diene-6,8-dione) were concentrated in vacuo to 15 mL and then put under N₂ atmosphere and 2.30 g (17.8 mmol) of octyl amine was added dropwise via syringe. The initial reaction was exothermic, and the mixture was subsequently stirred overnight at room temperature. The solvent was removed under vacuum (rotary evaporator), to give a gummy material, trituration with dilute HCl to gave a thick paste. An NaOH solution was added and stirred to dissolve the acid and then filtered to remove excess urea. The filtrate was neutralized with dilute HCl to give a white precipitate, which was filtered and dried giving 3.34 g (70.7%). m.p. 150-152°C. δ -¹H (DMSO-d₆): 11.93(1H, s), 8.98(1H, s), 7.96(1H, s), 7.49(1H, s), 3.22 (2H, t, J= 6.6Hz), 2.47 (1H, s), 1.10-1.80(12H, m), 0.81 (3H, t, J= 6.6Hz); δ -¹³C (DMSO-d₆) 165.575, 164.38, 127.69, 123.82, 115.616, 115.23, 30.97, 28.58, 28.42, 28.34, 26.23, 21.80, 13.633; IR(KBr): 3340.9, 2832.8, 1701.0, 1341.1, 1208.0, 1090.7, 651, 601.2, 526.6 cm⁻¹.

2-Octylpyrrolo[3,4-c]pyrrole-1,3-(2H,5H)-dione (5): To 3.10 g (11.6 mmol) of **4** in 15 mL of DMF (distilled from CaH₂) was added 2.5 mL of thionyl chloride while the

reaction mixture was cooled in an ice bath, under N₂ atmosphere. The red solution was stirred at room temperature for 2 hours. The reaction mixture was quenched in an ice/water mixture, saturated NaCl solution was added to the mixture and extracted 3 times with THF. The organic layers were combined and dried over anhydrous magnesium sulfate. Filtration and solvent removal on the rotary evaporator yielded an oil which was then subjected to high vacuum to remove the residual DMF. Chromatography of the residue on silica gel using ether:hexane::3:7 (v/v) , gave 2.52 g of a viscous liquid (86%). δ -¹H (CDCl₃): 10.05(1H, S), 7.08(2H, d, J= 2.4 Hz), 3.52 (2H,t, J=2.4Hz), 1.64 (m,2H), 1.22 (10H, m), 0.89 (3H, t, J= 7.01 Hz); δ -¹³C (CDCl₃): 165.0, 121.5, 116.0, 38.1, 31.7 , 29.1, 28.7, 26.9, 22.5, 13.9; IR(neat): 3303.2, 2928.3, 2858.5, 1753.4, 1693.5, 1585.2, 1544.0, 1437.4, 1387.3, 1061.8, 754.9, 590.5 cm⁻¹; MS: M⁺ = 248, 207, 177, 149 (M⁺ - C₇H₁₅), 122.

2-Octylpyrrolo[3,4-c]2,5-dibromopyrrole-1,3-(2H,5H)-dione (6). A solution of 0.80 g (3.2 mmol) of **5** dissolved in 20 mL of THF under N₂ atmosphere was cooled to -80°C (acetone/liquid nitrogen bath), and then 1.2 g (6.7 mmol) N-bromosuccinimide, was added , the mixture was stirred at -70°C for 30 minutes then at 0°C for 3.5 hours. A small amount (~ 0.1 g) of Na₂SO₃ was added, the solution stirred for 15 min., the reaction mixture was decanted and concentrated under vacuo. Then 20 mL of CCl₄ was added and the mixture stirred for 15 min. A precipitate (succinimide) had formed, was removed via filtration and filtrate washed with more portions of CCl₄. The filtrate was concentrated under vacuo to give 1.10 g of a dark green solid. Chromatography with 1:1::ether:Hexane (v/v) gave 0.60 g (46 %) of a light orange solid, m.p 100-103°C. δ -¹H

(CDCl₃): 10.32(1 H, s), 3.36 (2 H, t, J = 7.4 Hz), 1.63 (2H, m), 1.24 (10 H, m), 0.85 (3H, t, J = 6.6 Hz); δ -¹³C (CDCl₃): 161.9, 122.1, 97.7, 38.4, 31.8, 29.1, 28.6, 26.9, 22.6, 14.0; IR (neat): 3200.2, 2929.0, 2853.6, 1758.4, 1692.3, 1548.5, 1432.4, 1389.9, 1343.5, 1207.2, 754.3, 693.7 cm⁻¹.

Polymerization of 2-Octylpyrrolo[3,4-c]2,5-dibromopyrrole-1,3-(2H,5H)-dione. To 0.20 g (0.49 mmol) of **6** in 1 mL of DMF (distilled from CaH₂) was added 67 mg (1.02 mmol) of copper bronze under nitrogen atmosphere. The mixture was heated at 100-115°C for 4 hours. The reaction mixture became dark on heating. The mixture was quenched in ice/water and then extracted with 3 portions of diethyl ether. The organic layer contained a suspension which was filtered to remove the suspended solids. The filtrate was dried over magnesium sulfate. Filtration and solvent removal in vacuo provided a dark residue 0.08 g (67% yield). δ -¹H (CDCl₃): 7.27 (1H, s), 3.55 (2H, m), 1.8-0.8 (15H, m); δ -¹³C (CDCl₃): 164.8, 162.9, 125.3, 122.8, 121.9, 121.6, 120.2, 117.5, 117.4, 116.0, 97.5, 38.7, 38.5, 38.4, 38.3, 38.2, 31.8, 29.2, 28.8, 28.7, 26.6, 14.0; IR: 3433.0, 3182.5, 2925.8, 2853.7, 1757.4, 1692.7, 1588.5, 1546.5, 1433.6, 1389.4, 1344.4, 1258.4, 1212.1, 1098.6, 1017.4, 751.9, 692.9 cm⁻¹.

Further efforts to increase the molar mass proved unsuccessful. These included Sonigashira coupling of borate derivatives and the use of active nickel as a catalysts. The most probable cause for this is the reactive pyrrole hydrogen. Attempts to protect this site proved unsuccessful.

Microwave Enhanced Diels-Alder Formation of Heterocycles

Diels-Alder reactions as a tool for the synthesis of pyrrole, monomers, the building blocks.

This project was focused on the Diels alder reaction of hetero cycles as furans, pyrrole, imidazoles, oxazoles, and thiophenes:

We started the project with synthesizing 3, 4-substituted pyrroles, as shown in the scheme, we were able to make the polypyrroles oligomers, shown in the scheme. The work was published, Pollack et. al. ¹.

As the synthesis of the monomer required a multi-step synthesis we diverted our attention to the study of Diels-Alder reaction to provide the substituted pyrroles in a more convenient way.

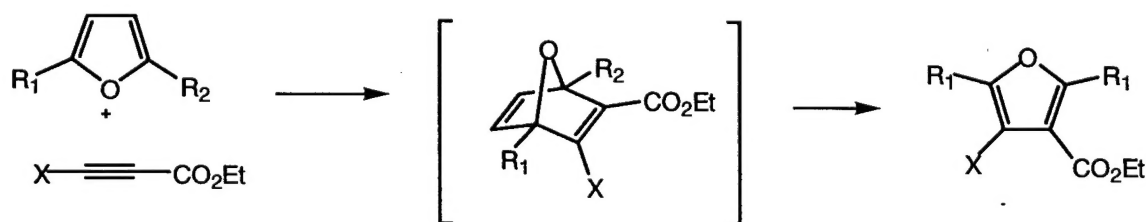
Reactions of N-substituted pyrrole with a variety of dienophiles was unsuccessful in our hands under conventional heating in toluene or neat. A dark mixture of product is obtained with a low conversion.

To investigate the Diels Alder reaction of the heterocycles we started with the readily available furan. Under conventional heating the reaction of furan, 2-methyl substituted furans, 2-silylfurans, were sluggish at about 110°C in refluxing toluene. Minor product or decomposition was noticed even with reactive dienophiles such as diethylacetylene

dicarboxylate (DEAD), ethylpropiolate, benzquinone, dibenaoylethylene, N-alky-
maleimide, and non reactive ones as β -nitrostyrene, 1-nitrocyclohexene. The reaction
were carried out for more than 24 hours.

Turning our attention to the microwave energy enhancement, as early reports by Majestic
and others showed that Diels-Alder reaction of furan with DEAD can go to completion in
10-15 minute in a sealed tube to give the adduct in good yields.

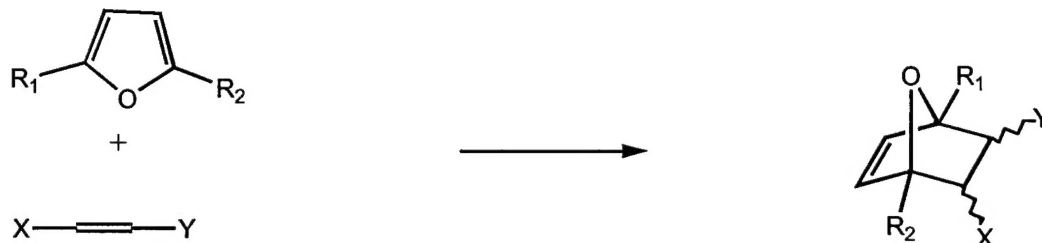
We repeated the same reaction in a commercial microwave oven in a capped vial, we
found that it proceed in few minute to give the adduct and the retro Diels-Alder adduct
mixture as the major components. Heating to about 15 minutes give the retro product in
very high yields as the sole product. This was very encouraging to test the other dienes,
as the products are of important functionality that will further manipulation of the
obtained furan to a variety of useful intermediates. Scheme II shows the conversion:



R1	R2	X	Time (min)	%yield
H	H	CO ₂ Et	10	83
H	H	H	20	76
H	Me	CO ₂ Et	20	71
H	SiMe ₂ Ph	CO ₂ Et	15	63

H	SoMe ₂ CH ₂ Cl	CO ₂ Et	30	trace
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Substituted olefinic dienophiles were investigated, The results are shown in Scheme III



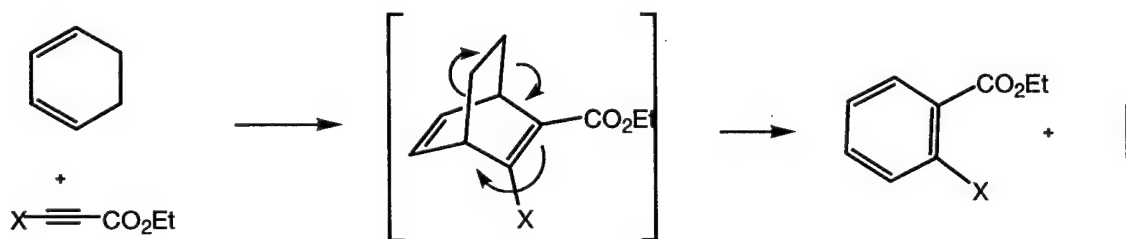
R1	R2	Dienophile	time	yield
H	H	Fumarate	10 min	83
H	H	Maleate	20	80
H	H	nitroStyrene	15min	63
H	H	Nitrocyclohexene	30 min	low yield
H	H	dibenzoylethylene		

As we noticed not much of reactivity was observed for olefinic dienophiles,. We attempted few Lewis acid to activate the reaction, Cerium trichloride, seemed to facilitate the reactions in some cases if combined with microwave heating. Some of the results are shown in scheme VI.

Diels alder reaction of imidazole with dienophiles was complicated by the formation of an adduct as soon as mixing the reagents, it was not clear if the adducts are Michael addition products or real Diels-Alder adduct. Further investigation in this type of dienes is needed.

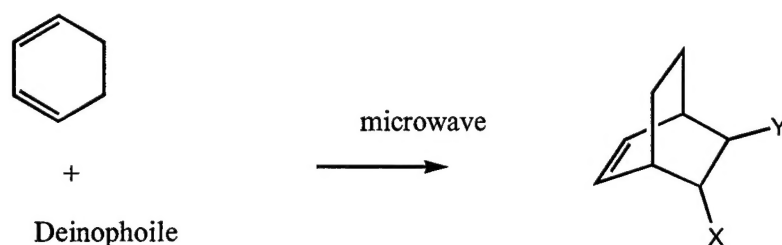
We were able to promote the Diels-Alder reaction of 1,3-Cyclohexadiene effectively with dienophiles using the microwave heating, and in some case in a combination with Lewis acids.

1,3-cyclohexadiene reacted with acetylenic dienophiles in 10-20 minutes to give the Diels alder adduct, which proceeded to lose ethylene via retro Diels-Alder to give the substituted aromatic compounds. The results are presented in table V.



X	Time	%yield
CO ₂ Et	10	94
H	10	92

1, 3-cyclohexa diene reacted with olefinic dienophiles under microwave heating only or catalyzed by lewis acid as shown in scheme VI:

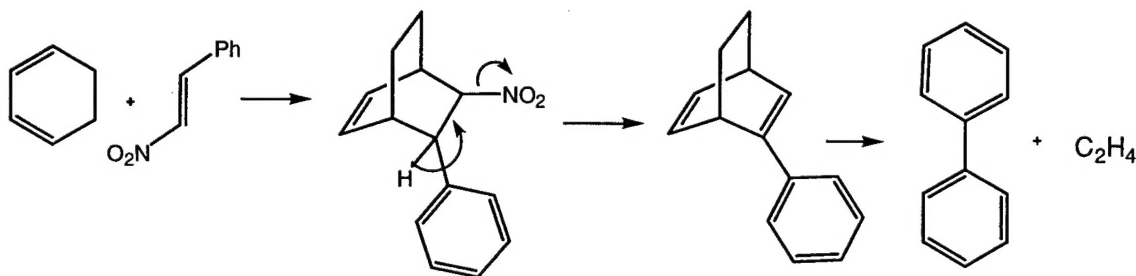


Dienophile	time	conditions	yield
N-Methylmaleimide	10 min	microwave	93, exo/endo
dimethylmaleate	16	Lewis acid/MW	98 exo/endo 6:4
Diethylfumarate	20 min	MW	80
Dimethylfumarate	20	Lewis acid/MW	96
trans-Dibenzolyethylene	20	MW	71
β -Nitrostyrene	20	Lewis acid/MW	80% biphenyl
cyclohexenone			
maleic anhydride	20	MW	91 Exo/endo

Scheme VI: 1, 3-Cyclohexadiene reaction with olefinic dienophiles

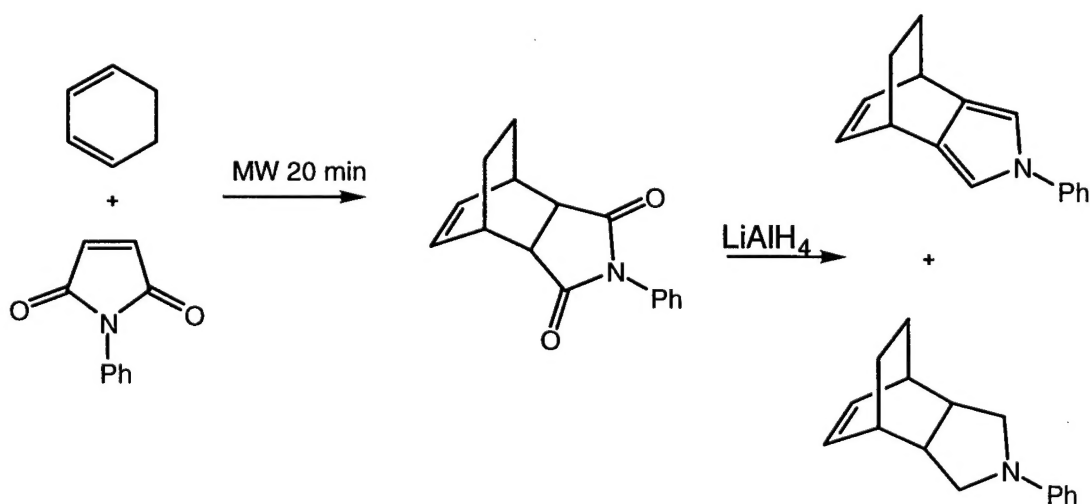
The reactions with 1,3-cyclohexadiene went smoothly to give excellent yields of the adducts. In cases where the yield was low or the conversion was low the lewis acid catalysis was productive.

In the case of β -nitrostyrene the adduct was not isolated, as a loss of nitrous acid was spontaneous followed by the loss of ethylene providing biphenyl. This conversion is shown in scheme VII :



Scheme VII: Mechanism for biphenyl formation from β -nitostyrene with 1,3-cyclohexadiene.

The products obtained from the N-Methyl maleimide were of of much interest as they constitute intermediates for the pyrroles we seeking. The substituted succinimides were reduced to a mixture of the corresponding amines and pyrroles. The reactions are shown in scheme VIII.



This process provides a route to the substituted pyrroles. We need to tune up the reduction of the succinimide products to provide either the amine or pyrroles. These compounds constitute a very useful intermediate for conductive pyrrole polymers, where the presence of the alkene provides a handle for further manipulation or cross linking. Up to this point the project was very successful, although it opens the door for further investigation into Microwave assisted reactions, and seeking a way for controlled reduction of succinimides.

We have published one paper and have few presentations. We are in the process of submitting three papers regarding the work presented.

Publication and presentations pertaining to this work:

1. S. K. Pollack, Y. M. Hijji, "Poly (2-alkyl-pyrrolo[3,4-c]pyrrole-1,3-(2H,5H)-dione-4,6-diyl). A novel Class of Intramolecularly Hydrogen-Bonded conjugated Polymers ", *Macromolecules*, 1997, 30, 6709-6711.
- 2.. Y. M. Hijji, J. Wenene and J. Fuller, and S. K. Pollack, 1999, Rimi 1st annual symposium, Atlanta, GA, March 18, 1999.
 - a) Y. M. Hijji, J. Wenene and J. Fuller, 2000, 221 ACS national meeting, Washington D. C. poster # ORG 428.
 - b.) Y. Hijji ; J. Wenene, Morgan State University Undergraduate and Graduate Symposium, 2000, poster # C-8

C) Y. M. Hijji, J. Wenene and J. Fuller, 2000, UMBC undergraduate research
symposium

d) Y. M. Hijji, J. Wenene and J. Fuller, 222, ACS national meeting, Sandiago, CA. April
2001.